UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
National Risk Management Research Laboratory
Water Supply and Water Resources Division
Cincinnati, Ohio 45268

REQUEST FOR ASSISTANCE (RFA)

MEASUREMENT OF FLUOROSILICATES IN DRINKING WATER

Announcement date: April 25, 2002

An offeror must submit the application (original plus four copies) so as to be received by **12:00 noon Eastern Daylight Saving Time on Monday, June 3, 2002.** The application should be addressed as follows:

Edward T. Urbansky
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Water Supply and Water Resources Division
26 West Martin Luther King Drive, MS 681
Cincinnati, Ohio 45268

An application received after the above time and date will not be considered unless there is clear evidence that the application was mishandled by EPA after its timely receipt.

Questions regarding this RFA should be directed by electronic mail to
urbansky.edward@epa.gov

Applicants will be notified by letter as to the disposition of their preapplication (accepted/not accepted) and informed of the identity of the successful proposal.

Proprietary Information: In accordance with 40 CFR 40.150, applications considered relevant to EPA research objectives will be viewed for technical merit by at least one reviewer within the EPA and at least two reviewers outside of the EPA. Therefore, proposals submitted in response to this competitive solicitation will not be considered if the applicant asserts a claim of confidentiality for technical information contained therein.

REQUEST FOR ASSISTANCE
Measurement of Fluorosilicates in Drinking Water

1.0. INTRODUCTION

The improvement of the quality of the nation's drinking water is an important goal and research to extend the boundaries of knowledge in this area is a function that government serves well. The Water Supply and Water Resources Division (WSWRD) of the National Risk Management Research Laboratory (NRMRL) is involved in a wide range of efforts, one of which is the review and advancement of the science on regulated contaminants. Much of the nation's drinking water is fluoridated, and fluoride is regulated by the EPA at a maximum contaminant level of 4.0 mg L^{-1}. The division has completed a review of the scientific literature and has identified certain areas for which additional information is desired. The division seeks to promote the public welfare by researching basic liquid aqueous phase solution chemistry of regulated contaminants and soliciting competent researchers capable of completing research projects that fill identified gaps in the scientific literature. To that end, the division seeks to fund a proposal on the measurement of fluorosilicate species in drinking water.

2.0. RESEARCH OBJECTIVES

2.1. Background

Hexafluorosilicic acid (H_2SiF_6) and sodium hexafluorosilicate (Na_2SiF_6) are the most commonly used fluoridating agents by potable water systems in the U.S. These species dissociate and hydrolyze to produce fluoride anion (F^-). The release of fluoride proceeds through a complex, multi-step equilibrium process that is not well-understood. A variety of models have been proposed, and the speciation remains a matter of debate as does the existence of some fluorosilicates. A review of the relevant chemical literature detailing the complexities, disagreement, and scientific facts has been prepared by the EPA. This review is available to prospective applicants, and they are encouraged to request a copy prior to preparing a proposal.

In addition to the silicon(IV) present from the fluoridating agent, many natural water supplies contain soluble oxo- and hydroxosilicates, which further complicates the speciation. The EPA seeks information on the utility of techniques and methods for monitoring the species formed during the dissociation and hydrolysis of hexafluorosilicate as well as those species present once equilibrium is achieved. These data are expected to aid in the development of pharmacokinetic and toxicokinetic studies and to further the understanding of the fate of fluoride, including its interactions with other species in drinking water. As such, the results of this study will be of use to state agencies, water utilities, and other governmental or scientific bodies who seek to ensure the quality of the nation's drinking water supplies.

2.2. Objective

The primary objective of this RFA is to investigate the reactions that take place when fluorosilicates are added to drinking water supplies and what concentrations of which fluorosilicate species may monitored in finished drinking water supplies and what techniques may be used for such monitoring. A secondary objective of this RFA is to explore what spectroscopic or other techniques are most amenable to determination of equilibrium constants for fluorosilicate systems, which engage in multiple, simultaneous, and complex equilibria. A tertiary objective is to consider what techniques might be applied to kinetic and mechanistic studies of the dissociation and hydrolysis of hexafluorosilicate. Conditions in finished drinking water include total fluoride concentrations on the order of 20 μM and total silicon(IV) concentrations on the order of 300 μM. Collaboration by skilled experimentalists with expertise in inorganic chemistry and the analytical techniques is encouraged.

2.3. Project design

The EPA envisions that a typical project proposal will include such sections as described below.

2.3.1. Literature review

A review of the chemical literature detailing the complexities, disagreement, and basic chemistry of fluorosilicate equilibria in aqueous solution has been prepared by the EPA. Prospective applicants are encouraged to request a copy of the EPA's review of the fluorosilicate literature prior to preparing a proposal. In their proposals, applicants should summarize key data and results from the chemical literature to demonstrate an understanding of the relevant chemical equilibria, the practical and theoretical challenges associated with the proposed investigation, proof-of-concept, and to clarify elements of the proposal. Footnotes should be used to cite relevant references.

2.3.2. Analytes and measurement conditions

A number of homoleptic and heteroleptic fluorosilicates have been proposed in the chemical literature, with a mixture of coordination numbers at the silicon(IV) center.

hexacoordinate: $HSiF_6^-$, SiF_6^{2-}, $Si(H_2O)F_5^-$, $SiF_5(OH)^{2-}$, $Si(H_2O)_2F_4$, $Si(H_2O)_3(OH)_2F^+$

pentacoordinate: SiF_5^-, $SiF_4(OH)^-$

tetracoordinate: $SiF_4(aq)$, $SiF_3(OH)$, $SiF_2(OH)_2$, $SiF(OH)_3$

tricoordinate: $Si(OH)_2F^+(aq)$

It is not known if all of these species actually exist or under what concentrations they might be expected to predominate. In order for utilities, public health, and other agencies to understand the fate of fluoride and fluorosilicates and to adjust water treatment parameters so as to provide the

highest qualitiy water, it will be important to determine what species exist (as opposed to those that may be or have been deduced from fits to potentiometric data) and to find techniques suitable for the measurement of these species in liquid aqueous solution. An important aspect of the proposal will be determining the conditions necessary (e.g., ratio of total fluoride concentration to total silicon(IV) concentration) for biasing the equilibria in order to measure specific fluorosilicate species.

2.3.3. Instrumental techniques and data requirements

For the analyte species in subsection 2.3.2, the successful proposal shall explain and describe how the investigators plan to obtain comparative data documenting the existence of fluorosilicate species in liquid aqueous solution using amenable techniques, such as ^{19}F nuclear magnetic resonance (NMR) spectrometry, Raman spectrometry, attenuated total reflectance Fourier transform infrared (ATR/FTIR) spectrometry. Chromatographic, electrophoretic, and mass spectrometric techniques will not be considered at this time as they perturb the equilibrium system. In addition, potentiometric and other electrochemical studies will not be considered as there are already considerable data available and the application of such techniques requires reliance on current equilibrium models or the generation of new models for which the speciation cannot be otherwise confirmed. The proposal shall identify the equipment/instrumentation to be used, its availability, and any collaborations or subcontracting required for its use.

Comparative data are desired for the advantages and disadvantages associated with various techniques. The kinds of information that will be useful to water utilities, public health, and environmental agencies include the following: calibration plots at concentrations relevant to drinking water, lower limits of detection; method detection limits (as defined by EPA); and dynamic ranges—in cases where the dynamic ranges are not linear, fits to smooth curves are most useful. Many of these species are suspected to exist at nanomolar, picomolar, or femtomolar concentrations, based on available equilibrium models. Not all techniques or methods will be able to reach such concentrations, and the objective is to discern the utility of various techniques for monitoring potable water supplies that might be applied in the field or in the laboratory.

3.0 SPECIAL REQUIREMENTS

3.1. Quality Assurance Requirements

From 40 CFR 30.503 (d): If your application is for research financial assistance, it must include a quality assurance narrative statement that either identifies and addresses the following area or provides justification why any of these areas do not apply to the proposal.

3.1.1. The intended use of the data and the associated acceptance criterial for data quality, i.e., precision accuracy, representativeness, completeness, and comparability

3.1.2. Requirements for precision, accuracy, representatives, comparability, and how these will be determined, e.g., instrument calibration, number of replicates, statistical tests and parameters

3.1.3. Sources of materials and standards, procedures for physical handling of solutions and materials, identification, preservation, transportation, and storage

3.1.4. Description of measurement methods of test procedures with statement of performance characteristics if methods are nonstandard

3.1.5. Standard quality assurance/quality control procedure [e.g., American Society for Testing and Materials (ASTM), American Public Health Association (APHA), American Water Works Association (AWWA) standard procedures, good laboratory practices] to be followed. Nonstandard procedures must be documented in detail.

3.1.6. Procedures for the analysis, reduction, reporting, and archiving of data, description of statistical analyses to be used

Following selection of the application and approval of the QA narrative statement, the successful applicant will be advised of the need to prepare a quality assurance project plan (QAPP). A QAPP is required and will be due to the project officer for approval at least 30 days before any data collection is initiated. Guidance is provided in the "Interim Guidelines and Specifications for Preparing guidance on the development of a QA plan is also provided in the NRMRL Pocket Guide "Preparing Perfect Project Plans," EPA/600/9-80/087, October 1989. The QAMS-005 document and the NRMRL Pocket Guide can be obtained from the project officer. Details on preparing the QAPP will be forwarded to the selected recipient.

3.2. Reporting Requirements

The application shall document how the following reporting requirements shall be met.

3.2.1. If selected, recipients shall report to the project officer by electronic mail. These reports shall be of an informal nature, but shall include documentation of progress (e.g., spectra, calibration plots, tabulated data) either by electronic or paper copy.

3.2.2. Recipients shall submit copies of all abstracts, conference proceedings, manuscripts submitted to journals, and other products shall be submitted to the project officer at the same time that these are submitted to conference, journal, professional society, etc.

3.2.3. Recipients shall submit a final report or, in lieu of a final report, evidence of acceptance of peer-reviewed journal articles that sufficiently satisfy the project's objectives and output.The decision to accept other documents in the place of a final report rests with the project officer.

3.3. Cost Information Requirements

The following cost information is required in the application to evaluate the offerors ability to successfully complete the research. Breakdown of the budget by year is required.

3.3.1. Personnel: Identify participants by title and institution along with percentage of time allocated to the project plus fringe benefits. Describe the role of each principal investigator and/or principal investigator's team.

3.3.2. Equipment: Identify all equipment to be purchased.

3.3.3. Supplies: Itemize if greater than 3% of total cost.

3.3.4. Travel: Specify purpose, project site, symposium, professional society meeting, etc.

3.3.5. Subcontracts: Specify nature of service contracted and itemized budget. EPA review of costs and services is required before awarding the project.

3.3.6. Collaborators: Identify collaborators with title, institution, and role.

3.3.7. Other Direct Costs: Specify training, disposal, permitting, etc.

3.3.8. Indirect Costs: Explain how indirect costs are calculated.

3.4. Proposal Length and Format

3.4.1. The proposal shall be divided into the following sections and presented in this order:

1. SF-424 (application for federal assistance)
2. Summary, 1 page
3. Introduction, 1-3 pages
4. Objectives, 1-2 pages
5. Timeline for meeting objectives and delivering outputs (preferably a figure), 1 page
6. Table of instrumental techniques and methods (including specific instrumentation, i.e., brand, model, etc.), 1-2 pages

7. Experimental design (reagents, conditions, equipment, procedures, etc.), 10 pages maximum

8. Data handling, quality assurance narrative report (see above), anticipated results/outputs (spectra, fractional distribution plots, tabulated detection limits, etc.), 10 pages maximum

9. Waste minimization/waste disposal strategy/environmental impact statement, 1 page or less

10. Summary of the role/contributions of each principal investigator's group, 1 page or less

11. Curriculum vitae of each principal investigator (limited to 2 pages per PI); include name, current position, current employer, education, recent experience/professional development, up to 5 related publications and up to 5 recent publications per PI.

12. SF-424A (budget information); include detailed budget information as outlined in subsection 3.3 immediately after the SF-424A.

13. SF-424B (assurances—non-construction programs)

14. EPA Form 4700-4 (preaward compliance review report for all applicants requesting federal financial assistance)

15. EPA Form 5700-49 (certification regarding debarment, suspension, and other responsibility matters)

3.4.2. Pursuant to EPA Order 1000.25, proposals shall be prepared on recycled paper and printed on both sides of the paper.

3.4.3. Proposals shall be prepared in 12-point Times or a similar serif typeface with one-inch margins and with spaces (double-spacing) between paragraphs. A single staple in the upper left corner shall be used to fasten pages. All pages shall be numbered consecutively.

4.0. SCOPE

The project period is two years. The EPA estimates that its share of the budget will be slightly under $100,000. EPA support may be incrementally funded across the life of the project with full funding expected at the beginning of the second year. EPA expects the recipient to share costs. Recipient participation is required and may be in the form of travel costs, NMR spectroscopy facilities, instrumentation already owned by the principal investigator(s), salaries, etc., and used to augment EPA's contribution.

5.0. AUTHORITY, FUNDING MECHANISM, GOVERNMENT INVOLVEMENT

This research is authorized under Section 1442 of the Safe Drinking Water Act. Pursuant to this authority, the EPA may make assistance agreements to public agencies and private nonprofit institutions. It is anticipated that the award from the request for assistance will be made in the form of a cooperative agreement because substantial participation by EPA is envisioned.

The EPA is engaged in a review of fluoride as a regulated contaminant. EPA scientists are expected to make significant contributions to the technical effort and have already reviewed the chemical literature. EPA participation in the technical aspects of the project, such as experimental design, data analysis, sample analysis, sample preparation and/or reagent selection, evaluation of results, and preparation of manuscripts will demonstrate substantial participation.

6.0. ELIGIBILITY

The response to this RFA is open to all qualified sources, including those that are identified as a result of EPA's Internet solicitation on its home page through June 3, 2001. Written questions will be accepted by the project officer and the responses sent to all qualified applicants.

A Grant Application Kit can be obtained from the EPA's website at the URL listed below: http://www.epa.gov/ogd/grants/how_to_apply.htm.

All required forms may be obtained from the EPA website as Adobe Acrobat portable document format (pdf) files or printer-friendly hypertext mark-up language (html) files. Further instructions are provided on the EPA website.

7.0. PROPOSAL REVIEW AND SELECTION CRITERIA

Proposals will be evaluated in accordance with the following weighted criteria:

7.1. Responsiveness to RFA (30%)

Proposal addresses RFA's directives and meets project objectives.

7.2. Scientific merit (40%)

Understanding of fluorosilicate equilibria and the complications of measuring concentrations homo- and heteroleptic fluorosilicates in drinking water matrixes is demonstrated.

Techniques and methods are valid for analyzing real or contrived drinking water matrixes. Special considerations have been made for interferences, experimental difficulties, forcing conditions, etc.

Design is such that it could accomplish objectives. There is a likelihood of accomplishing objectives.

7.3. Staff and facility qualifications (20%)

Staff credentials demonstrate ability to undertake scope of work and recognition in areas of inorganic chemistry and analytical chemistry.

Facilities and equipment are suitable for the application of these techniques and methods and represent the state of the science insofar as accomplishing project objectives.

7.4. Soundness of budget (10%)

Costs, supplies, rates, hours, etc. are reasonable in support of proposed work.

The evaluation will support the determination and selection of the recipient.

It is anticipated that peer review and agency review will be completed with 60 days from the closing date of this RFA.

The preparation of a cooperative agreement package for signature by EPA officials and then by the recipient will follow.